NOTE

Indian J. Phys. **70A** (5), 637–640 (1996)

IJP A
— an international journal

Debye-Waller factor and Debye temperature for three metal-organic complexes

G Nagendrappa*, R Somashekar, M S Madhava and P G Ramappa*
Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore-570 006, India

Received 30 October 1995, accepted 8 April 1996

Abstract : The X-ray Debye-Waller factors and Debye temperatures for three metal-organic complexes taken in the powder form have been determined by measuring integrated intensities of selected Bragg reflections at room temperature The characteristic specific Debye temperatures estimated from these values have been compared with theoretical values.

Keywords : Metal-organic complex, Debye-Waller factor, Debye temperature

PACS Nos. : 61.10.Nz, 63.70.+h

The X-ray Debye temperature θ_M can be evaluated from the measured X-ray diffractometer intensities at room temperature using the Debye model where one does not distinguish between the acoustic and the optical branches of the dispersion curves. The Debye temperature is given by the expression [1]

$$B = \frac{6h^2}{pm_a k_B \theta_M}\left(\frac{\phi(x)}{x} + \frac{1}{4}\right), \tag{1}$$

where $\phi(x) = \frac{1}{x}\int_0^x \frac{y\,dy}{[e^y - 1]}$ and $x = \theta_m/T$,

p is the number of groups, m_a is the mean molecular weight, k_B is the Boltzmann constant, h is the Planck's constant and T is absolute temperature. Using the Debye-Einstein model where we have a Debye temperature and an Einstein temperature, the expression for B is [2]

$$B = \frac{6h^2}{pm_a k_B \theta_m}\left(\frac{\phi(x)}{x} + \frac{1}{4}\right) + \frac{2(p-1)h^2}{pm_a k_B \theta_E}\left(\frac{1}{e^{x_L - 1} + 1/2}\right). \tag{2}$$

*Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore-570 006, India

In the classical limit, both have the same linear dependence and separation of these two temperatures is not possible, but it has been observed that [2] Einstein temperature should be $\sqrt{2}$ times smaller than θ_M.

(i) Sample preparation :

All the three complexes have been prepared by mixing ethanolic solutions of the respective metal salts and ligno caine salt in 1 : 2 stiochiometric ratio. The mixture was evaporated to small volume and the concentrated solution was kept undisturbed at room temperature for 20-30 hours. Separated crystalline complex was filtered and washed with diethyl ether and then dried in a dessicator over anhydrous silica gel. ^{1}H NMR spectra (60 MHz, Hitachi make) of the complexes indicate the structurally intact lignocainium ion in all the three complexes.

(ii) X-ray recording :

Crystals of the samples were obtained by slow evaporation of the solution and then they were powdered. These powdered samples were used for recording the X-ray diffractograms

Table 1. Debye-Waller factors, Debye temperatures, cell parameters and reflections used for the metal-organic complexes.

Compound	Cell parameters with reflections used	B in nm^2	θ_M in K	θ_E in K	θ_D in K
$CO(NCS)_4^{2-}$ $(C_{14}H_{23}N_2O)_2$	a = 13 9 A, b = 6.9 A c = 8 4 A, α = 94 9 β = 90 3, γ = 97.6 (011), (201), (021) (302), (014), (122) (032), (024), (142)	14.3 ± 0.2	25.6 $\theta_{theoretical}$ = 18.1	18.1	36.2
$(ZnBr_4)^{2-}$ $(C_{14}H_{23}N_2O)_2$	a = 21.3 A, b = 12.2 A c = 9.7 A, α = 98.6 β = 91.7, γ = 89.5 (110), (020), (401) (302), (501), (203) (022), (031), (420)	20 9 ± 0.2	19.6 $\theta_{theoretical}$ = 16.9	13.8	27 7
$(CoBr_4)^{2-}$ $(C_{14}H_{23}N_2O)_2$	a = 14.6 A, b = 8.3 A c = 13.7 A, α = 90.4 β = 90.1, γ = 89.7 (020), (111), (012) (211), (121), (302) (022), (240), (222)	32.8 ± 0.3	15.7 $\theta_{theoretical}$ = 16.8	11.1	22.2

at room temperature. For recording the X-ray diffractograms, X-ray powder diffractometer (JEOL, Japan) was used and a 2θ scan with a goniometer speed of 2° per minute with the following specifications was adopted : 35 kV, 15 mA, chart speed 40 mm/min, channel

width 50, channel center 100, range (cps) 400 and a time constant of 2. A simple multidimensional programe (SIMPLEX) written in Fortran (FTN77) language was used to identify all the observed reflections and hence to give a set of unit cell parameters $(a,b,c,\alpha,\beta,\gamma)$ which will fit the observed Bragg angles of the reflections to within ±1 percent of the mean value [3]. These parameters for all the samples are given in the Table 1. For all the samples, the reflections that are present and hence used for further analysis, are also given in Table 1.

X-ray intensities can be affected by the surface roughness and porosity of the sample. However, the error due to this factor is about 2% at $2\theta = 20°$ and is less at higher angles [2]. The relative integrated intensities were recorded over a 2θ range of 2° on either side of a peak and the background was estimated by a straight line.

To a first approximation, let B be the mean-Debye-Waller factor for metal-organic complex and the integrated intensity for this complex is given by

$$\langle I \rangle = KL_pP\left(\sum f\right)^2 \exp(-2B\sin^2\theta/\lambda^2). \tag{3}$$

Here K is a constant, L_p is Lorentz polarization factor, P is the multiplicity factor, θ is the Bragg angle, λ is the wavelength of the X-rays and B is the mean Debye-Waller factor for the sample. The atomic scattering factors given in international tables [4] have been used to compute $(\sum f)^2$.

If follows from eq. (3) that a graphical plot of ln $\left(\frac{<I>}{KL_pP(\Sigma f)^2}\right)$ against $\frac{\sin^2(\theta)}{\lambda^2}$ is a straight line and the least-squares method has been used to determine the slope and also standard deviation from which the temperature factor B is obtained. Using this value in eq. (1) and the published value [5] of $W(x)$ for various x, we have determined θ_M for the Debye model. θ_E for the Debye-Einstein model is given by $\theta_M/\sqrt{2}$. The specific heat Debye temperature is given by $\theta_D = p^{1/2}\theta_M$, where p is the number of groups [2]. The present values of cell parameters, reflections used for determining the Debye-Waller factor, Debye tempertures θ_M, θ_E and standard deviation are given in Table 1, for all the three compounds. Using crystal data reported here for the samples at room temperature, the Debye temperature calculated using

$$\theta_{\text{theoretical}} = C\left(\frac{T_m}{MV^{2/3}}\right)^{1/2}, \tag{4}$$

are also given in Table 1. Here, ($C = 115$) [6] is a constant dependent on the structure, T_m is the melting temperature, M is the mean molecular weight and V is the mean molecular volume. Here, it should be mentioned that these complexes do not have a sharp melting point. In fact, we have taken the clearing point temperature wherein the sample forms isotropic liquid.

Acknowledgment

Authors thank Dr. U D Prahllad, Central Instrument Service Laboratory, University of Mysore, for the assistance in X-ray diffractometer recordings.

References

[1] K G Subhadra and D B Sirdesmukh *Pramana-J. Phys.* **9** 223 (1977)

[2] R D Horning and J C Staudenmann *Acta. Cryst.* **A44** 136 (1988)

[3] W Press, B P Flannery, S Teukolsky and W T Vettering *Numerical Recipes* (UK : Cambridge University Press) p 289 (1986)

[4] *International Tables For X-ray Crystallography* (UK : Kynoch) **Vol. 1–3** (1969)

[5] G C Benson and E K Gill *Table of Integral Functions* (Ottawa, National Research Council of Canada)

[6] F Lindemann Z. *Phys.* 1 609 (1910)